

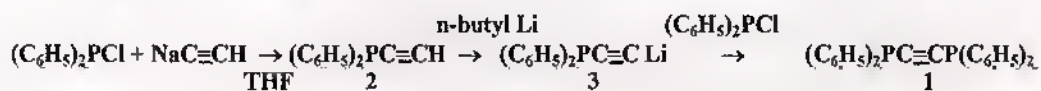
An Improved Method for the Preparation of Bis-Diphenylphosphino Acetylene and unsymmetrical Aryl Substituted Diphenylphosphino Acetylenes

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Abstract

The conventional method for preparation of bis-diphenyl phosphino acetylene (**1**) involves reaction of two moles of diphenyl chlorophosphine with the di Grignard of acetylene. This method gives low yields, due to impurities and moisture in the acetylene and incomplete conversion to the di Grignard. We have developed a modified procedure involving reaction of diphenylchlorophosphine with commercially available powdered sodium mono acetylide in THF, giving diphenylphosphino acetylene (**2**). Reaction *in situ* of **2** with one equivalent of n-butyl lithium in hexane gives the mono lithium adduct (**3**), which on treatment with a second mole of diphenyl chlorophosphine gives **1** in ~80% yields. This method avoids purifying and working with acetylene gas, and also allows greater flexibility for the synthesis of unsymmetrical bis-diaryl substituted phosphino acetylenes, by employing the above sequence with differing diaryl substituted chlorophosphines.



Procedure for the Preparation of Bis-Diphenylphosphino Acetylene, 1

A 5 L three neck flask, equipped with mechanical stirrer, water condenser, calcium chloride drying tube, "Y" tube, N₂ inlet, heating mantle and 1.0 L pressure equalized dropping funnel, was charged with 1 L dry THF and 50g (1.04 mol) powdered n-butyllithium. The mixture was heated to reflux with stirring and 219g (196ml, 1.0 mol) diphenylchlorophosphine was added dropwise over one half hour. Refluxing was continued for an additional hour to generate monoalkyne intermediate 2, then the reaction was cooled to room temperature. The dropping funnel was charged with 1000 ml (1.0 mol) of 1M n-butyllithium in hexane, which was added dropwise with stirring over one hour with no external heating, generating monolithium salt 3. An additional 196 ml (1.0 mol) diphenylchlorosilane was charged to the dropping funnel and the pot heated to reflux. The second portion of diphenylchlorosilane was added dropwise over approximately one half hour, then refluxing was continued for an additional hour.

The heating was then discontinued and the reaction fitted with a Cloisen head, thermometer, water condenser, 2 L distillate receiving flask and outlet to a water aspirator. The organic solvents were removed under water vacuum with gentle mantle heating and the pot residue cooled to room temperature. 1 L water was added with stirring to dissolve salt byproducts, and stirring continued for 15 minutes. The solid crude 1 was collected by suction filtration, washed three times with 100 ml portions of water, and air dried overnight. Wt crude 1, 347g (88%) mp 75-80° C. Recrystallization from benzene afforded 249g (63%) Bis-Diphenylphosphino Acetylene, 1, mp 85-7° C,

Lit: mp 86-8° C